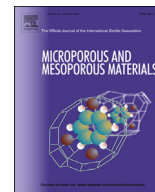




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Cation–anion double hydrolysis derived mesoporous mixed oxides for reactive adsorption desulfurization

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ABSTRACT

Mesoporous ZnO–Al₂O₃ mixed oxides (MO) were synthesized by double hydrolysis method at different temperatures and used as the support for the preparation of Ni/MO adsorbents. The reactive adsorption desulfurization (RADS) performance of adsorbents was evaluated in a fixed bed microreactor using thiophene as a model compound. The adsorbents before and after RADS were characterized by X-ray diffraction, N₂ adsorption/desorption, thermogravimetric analysis, Fourier transformed infrared spectrometry and transmission electron microscopy techniques. Results show that Ni/MO samples exhibited much higher RADS activity and larger accumulative sulfur capacity than sample NZA-K prepared using the conventional kneading method. The desulfurization activity of Ni/MO adsorbents decreased with increasing the crystallization temperature of MO. As a result, sample Ni/ZnO–Al₂O₃–60 °C synthesized at 60 °C showed the best desulfurization performance among all Ni/MO adsorbents. Detailed characterization results revealed that the high dispersion of NiO and ZnO, the absence of inactive NiAl₂O₄ and high concentration of surface Lewis acid sites may account for the superior RADS performance of Ni/MOs samples. Furthermore, based on the experimental results, a mechanism is proposed for the RADS process with Ni/MO adsorbents.

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1. Introduction

Reduction of sulfur content in transportation fuels is an important route for improving air quality. As new environmental regulations exert more stringent requirements on the sulfur content in oil fuels, researchers and refineries are faced with great challenges and are forced to develop efficient processes for producing cleaner fuels [1–3]. For instance, Euro V standards of transportation fuels stipulate sulfur level in gasoline to be less than 10 ppm. To meet new regulation requirements for the production of ultra-low sulfur gasoline, new and efficient desulfurization techniques are desirable and gaining increasing attention [4–6]. Taking China as an example, about 80% of the gasoline pool comes from FCC gasoline at present, which is responsible for the origin of 90% of total organosulfur compounds in gasoline [7]. Currently, in refineries, hydrodesulfurization (HDS) is commonly used to remove

sulfur from FCC gasoline. However, the conventional HDS process has intrinsic disadvantages. FCC gasoline contains high concentration of aromatics and olefin compounds, which ensures the satisfactorily high octane number of the liquid fuel. However, these compounds can be saturated during the HDS process, causing a loss in octane number [8–10]. In order to achieve ultra-deep desulfurization of FCC gasoline and preserve the octane value at the same time, several novel techniques have been proposed recently to produce low-sulfur content gasoline. Apart from traditional HDS, several non-HDS-based desulfurization techniques such as adsorption and reactive adsorption desulfurization [6,11], oxidative desulfurization, bio-catalytic treatment, extraction using ionic liquids etc., have been applied to remove sulfur from liquid fuels [12]. Among these methods, reactive adsorption desulfurization (RADS) is considered to be one of the most effective technologies for deep desulfurization because it combines the advantages of both HDS and adsorption desulfurization (ADS) techniques [13–17]. Conoco Philips Petroleum Co. developed a S-Zorb process which was based on reactive adsorption desulfurization with solid Ni/ZnO adsorbents at an elevated temperature under a low H₂ pressure [18,19]. In the RADS process using Ni/ZnO adsorbent, it has been reported

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that, in the initial step, nickel catalytically breaks the C–S bonds in the organosulfur compounds under H_2 and reacted further with sulfur to form Ni_3S_2 , which then reacted with ZnO to form ZnS and nickel was regenerated [20–22]. Huang et al. [23] examined the sulfur transfer mechanism in RADS process using K-edge X-ray absorption near-edge structure (XANES) and XRD techniques, which confirmed the formation of Ni_3S_2 intermediate. Furthermore, Bezverkhyy et al. investigated the reaction kinetics of thiophene on Ni/ZnO by thermal gravimetric analysis and suggested a three-step RADS mechanism. In the first step, thiophenic sulfur reacted with surface Ni to form Ni_3S_2 and then sulfur atoms in Ni_3S_2 reacted with H_2 to form H_2S in the next step. In the third step, H_2S diffused through the surface of ZnO to produce ZnS. The kinetics of these steps depends on the reaction conditions [17].

In the preparation of RADS adsorbents, a kneading method is commonly used. Wang et al. [8] studied the influence of sulfur concentration on the RADS performance of Ni/ZnO–SiO₂–Al₂O₃ materials synthesized using kneading method, and it was found that increasing sulfur content (more than 239 ppm) in feedstock dramatically decreased the desulfurization activity with a breakthrough sulfur capacity of 25.2 mg/g obtained. In another report, Meng et al. [24] investigated the effect of higher sulfur concentration (2000 ppm) on the performance of Ni/ZnO–Al₂O₃–diatomite adsorbents synthesized by the kneading method and found that thiophene conversion decreased quickly to less than 60% after 15 mL flow of feedstock with a low sulfur capacity typically below 10 mg S/g. It has been recognized that the presence of small and well dispersed ZnO particles is a key factor to achieve a satisfactorily high RADS activity [24,25]. Since the adsorbents prepared by the kneading method is simply a physical mixture of ZnO, SiO₂, and Al₂O₃ oxides, the compromised dispersion of ZnO and Ni may account for the poor performance of the adsorbents.

In order to achieve a good RADS performance especially when treating feedstock with a high sulfur concentration, novel approaches to the high dispersion of ZnO and Ni are desirable. Mixed oxides (MO) with high active component dispersion and excellent resistance to coke formation and thermal sintering, have gained much attention in the applications as catalyst supports [26]. We have previously established a cation–anion double hydrolysis (CADH) technique for the generalized synthesis of mesoporous mixed metal oxides. A series of mixed oxides were prepared with high surface area and high thermal stability. Especially, the active components were highly dispersed in the inorganic framework of another metal oxide even at exceptionally high loadings, which is advantageous compared with the conventional wet impregnation method [26–28].

In this work, a series of mixed oxides (ZnO–Al₂O₃) were synthesized at different temperatures using the CADH method. The physicochemical properties of adsorbents were studied with a variety of techniques. The RADS performance of MO-based adsorbents was evaluated in the reactive adsorption desulfurization of a model fuel and compared with that of the adsorbent prepared using the conventional kneading method.

2. Experimental

2.1. Chemicals and feedstock

Zn(NO₃)₂·6H₂O, ZnO, Ni₂O₃, pluronic P123 and sodium aluminate of analytical reagent grade were purchased from Sinopharm Chemical Reagent Co., Ltd. Ni(NO₃)₂·6H₂O was purchased from Shanghai Chemical Reagent, Hanson. All chemicals were used as received. In order to investigate the RADS performance of the adsorbents at high sulfur concentration, the model fuel was prepared by adding thiophene (analytical grade from Aldrich) as a sulfur

source in n-octane (analytical grade from Aldrich) to obtain a mixture with a sulfur concentration of 2000 ppm.

2.2. Preparation of mixed oxides (MO)

ZnO–Al₂O₃ MOs were prepared by the CADH method following our published procedure with modifications [26]. In a typical synthesis, an aqueous solution of Zn(NO₃)₂·6H₂O (2.97 g) and 2.23 g of pluronic P123 surfactant were prepared in 30 mL deionized water. 20 mL clear solution of sodium aluminate (3.28 g) was added dropwise into the first solution under continuous stirring and the mixture was kept stirring for 4 h. Subsequently, the reaction mixture was transferred into an autoclave with Teflon-line for crystallization at 60, 80 and 110 °C for 24 h respectively. The products were filtered, washed with deionized water, and dried at 80 °C in a vacuum oven for 12 h. Finally, all the prepared mixed oxides were calcined at 500 °C for 3 h in air in a muffle furnace. Samples obtained were labeled as ZnO–Al₂O₃–X°C, where X is the crystallization temperature of the mixed oxides.

2.3. Preparation of Ni/MO adsorbents

The Ni/MO adsorbents were prepared by an ultrasonic-aided incipient wetness impregnation method (IWI–U) using MOs as supports. 0.5 g of Ni(NO₃)₂·6H₂O was dissolved in tetrahydrofuran (THF) to prepare a Ni precursor solution [29], which was then mixed with MOs supports under ultrasonic sonication at 50 °C for 3 h. The obtained solid was dried at 80 °C overnight and calcined at 500 °C for 2 h. The adsorbents obtained were labeled as Ni/ZnO–Al₂O₃–X°C.

2.4. Reactive adsorption desulfurization

RADS experiments were performed in a fixed bed reactor with a stainless steel column having an internal bed dimension of 8 mm and a length of 250 mm. Fig. 1 shows the schematic diagram of the RADS reaction system with six sections: oil and gas inlet section, a stainless steel column reaction zone, product separation and collection section, pressure/temperature control section and exhaust gas section. Ethyl alcohol was introduced into the reactor and continuously flowed for 24 h followed by purging with pure nitrogen gas for 30 min to clean up the whole system. 1 g of adsorbent was introduced at the center of stainless steel column. Prior to RADS reaction, the adsorbent was reduced by H_2 gas with a flow rate of 40 mL/min under 0.5 MPa at 400 °C for 4 h. After the reduction of adsorbent, the reactor temperature was decreased to 350 °C and reaction system was pressurized to 1.5 MPa by H_2 . During the reactive adsorption desulfurization, the preheated feedstock was mixed with H_2 and injected into the reactor column by microinjection pump with a weight hourly space velocity (WHSV) of 4 h^{–1} and H_2 /Oil volume ratio of 400. The effluent liquid products were collected and cooled in a cryogenic trap in ice water bath and analyzed using Gas Chromatograph (BRUKER 450–GC) coupled with a PFPD detector. The accumulative sulfur capacity of adsorbents was calculated according to the method described elsewhere [30]. For comparison purpose, a Ni/ZnO–Al₂O₃ based adsorbent was prepared by the kneading method reported elsewhere [24]. In a typical procedure, Ni₂O₃, ZnO and γ -Al₂O₃ having the same molar composition to that of Ni/MO adsorbents were mixed together to form a homogeneous mixture. Then, a dilute HNO₃ solution (1 M), a peptizing agent, was added to make slurry, which was dried at 110 °C and calcined at 500 °C for 2 h. The sample thus prepared was denoted as NZA–K. The sample NZA–K was evaluated in the RADS under identical conditions as the Ni/MO samples.

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